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PAPER

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Tailoring the interface using thiophene small molecules in TiO_2/P3HT hybrid solar cells†

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In this paper we focus on the effect of carboxylated thiophene small molecules as interface modifiers in TiO_2/P3HT hybrid solar cells. Our results show that small differences in the chemical structure of these molecules, for example, the presence of the $–CH_2–$ group in the 2-thiopheneacetic acid (TAA), can greatly increase the TiO_2 surface wettability, improving the TiO_2/polymer contact. This effect is important to enhance exciton splitting and charge separation.

Introduction

The use of polymers in solar cells has revolutionized the development of flexible electronic devices. Combining polymers with electron acceptors based on inorganic semiconductors is an interesting approach because of the unique properties of nanocrystals, such as high electron mobility and gap tunability. Hybrid solar cells present interesting device architectures for the development of low-cost photovoltaic solar cell technology, as an alternative to entirely organic based devices.[1–4] In this context, CdSe, PbSe, ZnO and TiO_2 nanoparticles have already been applied with promising results.[5–7]

The use of TiO_2 as an electron acceptor is advantageous due to its low toxicity, high electron mobility as well as facile fabrication and well-known physical and chemical stability. Dye-sensitized solar cells, another type of third generation photovoltaic architecture commonly based on this oxide, currently show efficiencies exceeding 12%.[8,9] By coupling TiO_2 with hole conducting polymers such as poly(3-hexylthiophene) (P3HT), hybrid solar cells have been assembled in a bulk heterojunction architecture, giving an efficiency of 2.2%.[10] In the beginning, however, the efficiencies were less than 1%. Such efficiency increment was possible because of an improvement in charge separation, material's compatibility, minimization of recombination and an increase in hole mobility as a consequence of polymer orientation induced by the inorganic material.[11,12]

Optimization of the TiO_2/polymer interface is another approach towards hybrid solar cells with better efficiencies. Optimizing the interfaces, we can expect an enhancement of the exciton splitting, which is inhibited because of the hydrophobic nature of the polymer and hydrophilic nature of the TiO_2.[1,3]

Improvements in device's efficiency were observed with the use of modified polymers with polar groups or dye molecules. Using this approach, Bhongale and Thelakkat investigated the use of carboxylated polythiophene bound to the surface of titania nanorods, giving rise to an efficiency (η) of 0.79% with Cu phthalocyanine dye containing ether side chains and 1.19% with the thiophene oligomer oligo-3HT-(Br)COOH.[3] Another approach involves the use of small organic molecules with carboxylic groups that can be easily anchored to the oxide surface, increasing the hydrophobic/hydrophilic compatibility. These modifications can assist charge separation and also improve light harvesting, allowing an efficient transport and injection of charge carriers between TiO_2 and the polymer.[1,2,10,13–15]

Since in the most widely used cell geometry holes are collected at the front electrode, the combination of materials generates a non-ideal layer, where the polymer structure below the metal oxide creates a non-rigid ground. Thus, the use of inverted solar cells represents a conceivable option to improve the morphology control, where using TiO_2 films can be a good way to improve the solar cell performance through the ability to produce rigid paths for photogenerated electrons.[16] Thus, the electrons are rapidly injected into the film metal oxide and collected by the front contact through a highly ordered structure. Furthermore an electron selective front contact allows the usage of a noble metal with long-term air stability.[17]

Although inverted solar cells endue beyond 5% for a combination of TiO_2, P3HT and Sb_2S_3,[18] and for TiO_2, dye and 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenyl-amine)-9,9′-spirobifluorene, called as spiro-MeOTAD,[19,20] this type of configuration cannot yet compete with classic dye-sensitized solar cells (DSSC) and all-organic solar cells (OSC). This is not because the concept is incorrect, nevertheless the realization of the optimized cells is far from ideal.[17] Also, the optimal modifier is still unknown, even though the desired properties

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can be listed as a material able to improve the organic–inorganic interface and maximize the conversion of photons to charges, combined with a low charge recombination.[21]

Therefore, this work represents an effort to study the insertion of thiophene molecule derivatives as interface modifiers, focusing on the effect of these molecules on hybrid solar cells using an inverted configuration.

Experimental

Fluorine-doped tin oxide (FTO) coated glass substrates were first cleaned in an ultrasonic bath for 10 min, using water-detergent, ethanol and 2-propanol as solvents. They were then dried in air followed by 30 min of ozone treatment. For the devices, FTO substrates were cut into square pieces of 2.5 cm × 2.5 cm and the extremities were chemically etched away. A TiO_2 compact layer (50–80 nm) was deposited by spin coating a solution of titanium(IV)-isopropoxide (reagent grade, 97%), ethanol and acetylacetone at 5000 rpm for 1 minute, followed by drying in air for 5 min These films were then heated at 450 °C for 20 min. A second layer of mesoporous TiO_2 (~500 nm) consisting of a commercial TiO_2 suspension (T37, Solaronix) in ethanol (1 : 1) was spread onto the film by spin coating at 7000 rpm for 1 minute, and was heated at 450 °C for 40 min.

The electrodes were immersed in a 0.1 mol L^{-1} solution of the modifiers (chemical structures shown in Fig. 1) 2-thiophenecarboxylic acid (TCA), 2-thiopheneacetic acid (TAA) and 2,5-thiophenedicarboxylic acid (TDA) in ethanol for 16 hours.

To measure the contact angle, a small aliquot of water was dropped onto these films and images of each sample were obtained with a Theta Optical Tensiometer (Attension). Pictures were taken after making sure that the water drop was stabilized.

In order to assemble the solar cell devices, TiO_2 modified films were dipped for 30 min in diluted P3HT solution (chlorobenzene at a concentration of 3 mg mL^{-1}), then annealed at 50 °C for 5 min. Two additional layers of P3HT were deposited using a concentrated solution (16 mg mL^{-1}) by spin coating at 2000 rpm for 1 min followed by annealing at 100 °C for 10 min.

A PEDOT:PSS layer was spin coated over the active layer (2000 rpm for 1 min, resulting thickness ~30 nm). The commercial solution was modified by the addition of a suitable surfactant (Zonyl FS300 from Baytron) with a ratio of Zonyl : PEDOT:PSS equal to 1% w/w. The samples were annealed at 120 °C for 20 min. The metal contact (80 nm Au) was deposited by ultra high vacuum evaporation (~10^{-6} mbar). All these steps were carried out in a glove box. The device configuration is shown in Fig. 1.

I–V measurements were carried out with an ABET 150 W Xe lamp equipped with an adequate set of filters to achieve a solar spectrum of 1.5 AM G (intensity adjusted to 100 mW cm^{-2} using a calibrated Si photodiode), a Keithley model 2600 digital source meter and homebuilt Labview software.

The charge transfer properties of the films were evaluated by transient absorption spectroscopy, using an experimental configuration where the excitation by a nitrogen-pumped dye laser was set to 550 nm with a ~1 Hz pulse and the probe wavelength generated by a tungsten lamp was set to 980 nm. Data resulted from averaging 100–1000 laser shots. The absorption spectra were obtained on a Diode Array Spectrophotometer Hewlett Packard 8452A.

The images from field-emission scanning electron microscopy (FEG-SEM) were obtained in a JEOL JSM 6340 F equipment operating with 5 kV of tension and current of 12 μA. The samples were analyzed in a metallic holder covered by carbon using a Bal-Tec MD 020 by the sputtering technique at Centro Nacional de Pesquisa em Energia e Materiais (CNPEM).

Molecular modelling was carried out using the Hyperchem package using the DFT method with a 6-311G** orbital basis set and exchange correlation B3-LYP.

Results and discussion

Fig. 2 shows the *I–V* current–voltage curves for TiO_2/polymer hybrid solar cell devices assembled with and without the interface modifiers TCA, TAA and TDA. Comparing with the device where no TiO_2 interfacial modifier was added, we observe an increase in both short circuit current and open circuit voltage.

The control device without any TiO_2 modification showed the smallest open circuit voltage (V_{OC}), probably because of a high recombination rate. This result is consistent with other studies reported in the literature,[21,22–24] where TiO_2/P3HT devices have also displayed low V_{OC} values. The insertion of TDA molecules leads to a deterioration in the solar cell photocurrent. This can be related to poor charge separation at the TiO_2/polymer interface considering the hydrophilic character of the TDA molecule with its two carboxylic groups. TAS and water contact angle measurements will support this observation.

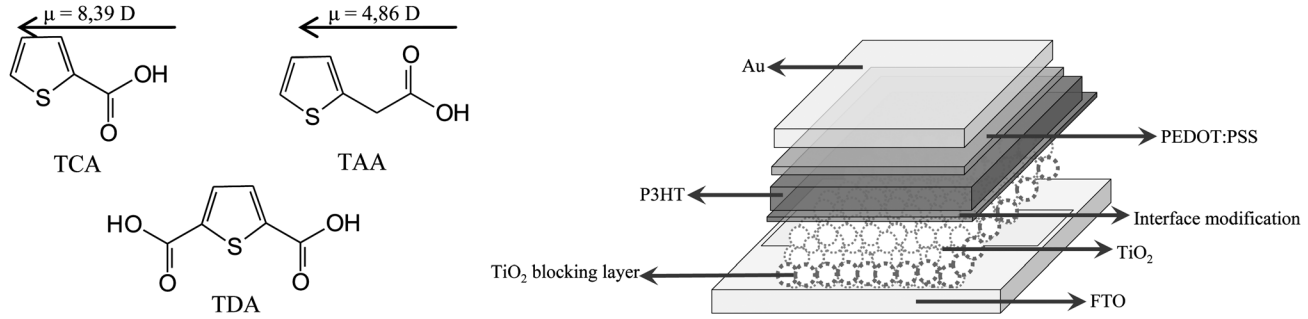

Fig. 1 Chemical structures of 2-thiophenecarboxylic acid (TCA), 2-thiopheneacetic acid (TAA), 2,5-thiophenedicarboxylic acid (TDA) and a schematic configuration of an inverted solar cell assembled in this work.

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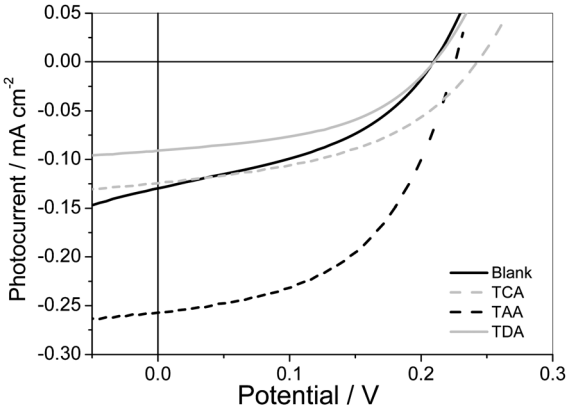

Fig. 2 *I–V* characteristics of TiO_2/P3HT inverted solar cells without modification (black solid line) and with TCA (gray dashed line), TAA (black dashed line) and TDA (gray solid line) surface modification, under 1 Sun simulated light AM 1.5 (100 mW cm^{-2}).

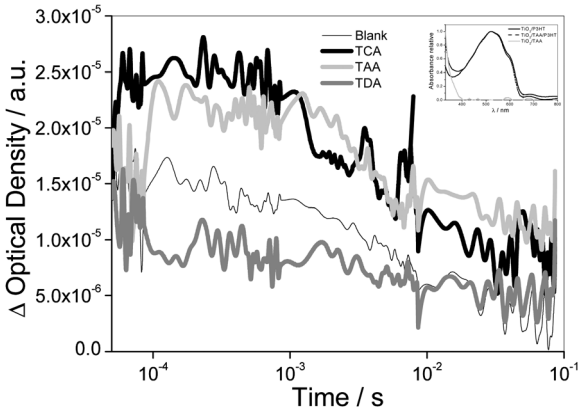

Fig. 3 Transient absorption spectra (TAS) for films with the configuration glass/TiO_2/P3HT (thin black line) and glass/TiO_2/modifier/P3HT, where the modifier corresponds to TCA (thick black line), TAA (thick light gray line) and TDA (thick gray line). The inset shows the absorption spectra of TiO_2/TAA (gray line), TiO_2/P3HT (black line) and TiO_2/TAA/P3HT (black dashed line). The TAS measurements were conduct under open-circuit conditions.

Interface modifications with TCA and TAA molecules lead to an increase in solar cell efficiency. In these devices, the increase in V_{OC} after surface modification either by TCA or TAA molecules can be attributed to the reduced recombination of charge carriers at these interfaces.[1,25] This effect is greatest when the TCA modifier is used, and the V_{OC} in this case increases from 200 mV to 240 mV, leading to an increase in efficiency from 0.01% to 0.03% compared with the solar cell without any modification. In addition, the higher V_{OC} values obtained with TAA and TCA might indicate changes in the semiconductor work-function. Changes in the interfacial dipole are well reported in the literature for the class of *para*-substituted benzoic acids and show that the dipole directed away from the titania causes an increase in V_{OC} (see Fig. 1 for more details about dipole direction).[15,26,27] In our study, both dipoles are set away from the titania and the magnitude is about double for the TCA case (8,39 D) in comparison to TAA (4,86 D), leading to higher V_{OC} values when the first modifier is applied in the solar cells. Besides, using TAA modification, the improvement in the photocurrent values is from 0.13 to 0.26 mA cm^{-2}.[16]

In order to further investigate the effect of the surface modification, laser transient absorption spectroscopy (TAS) was carried out on the time scale from 10^{-5} to 10^{-1} s. TAS can monitor the recombination between the TiO_2 electrons and the oxidized donor species[28–31] by following excitation at the P3HT absorption at 550 nm and probing the cationic P3HT long-lived excited states (polarons) at 980 nm.

As observed in Fig. 3, the data indicate that the best performance with TAA and TCA modification is related to the increase in the initial amplitude signal for these samples, where decays are attributed to the recombination between electrons in the TiO_2 conduction band with P3HT polarons rather than to P3HT triplet states.[32]

The bigger TAS signal for TCA and TAA modifications in comparison to TDA and pristine TiO_2 reveals a better charge separation and an increase in polarons yield. This is an indication that, in fact, the surface modification with these two molecules improves TiO_2/polymer contact and also exciton splitting. In this case, the light absorption by the TAA layer is negligible as shown in the inset in Fig. 3. The TiO_2 film with and without TAA has similar absorption profiles while it has a small difference in the presence of the P3HT layer below 400 nm. The spectrum presented no shift of the polymer absorption band, representing a superposition of the P3HT and TiO_2 spectra between 400–650 nm and below 400 nm, respectively,[32] where the small TAA concentration at the interface layer does not affect the light absorption properties. The slightly higher amplitude of the initial signal for the TCA modifier might be explained as because TAS were recorded under open circuit conditions and the recombination rate seems to be higher for TAA (in fact, the modification with TAA gives rise to lower V_{OC}).

To evaluate the compatibility of the polymer/nanoparticle interface, measurements of water contact angles were carried out to quantify the wettability of the modified films. Fig. 4 displays the contact angle images using different molecule modifications for the configuration FTO/TiO_2. It is expected that the small organic molecules could orient the carboxylic group to the TiO_2 surface while the thiophene rings are directed in the opposite direction.

In fact, the images demonstrate that the organic interface modification changes the surface character, indicating a variation in the TiO_2 surface hydrophobicity. For the TCA and TAA modifications, the contact angles were found to be 14.41 ± 0.45 and 16.90 ± 0.27, respectively. Interestingly, the additional

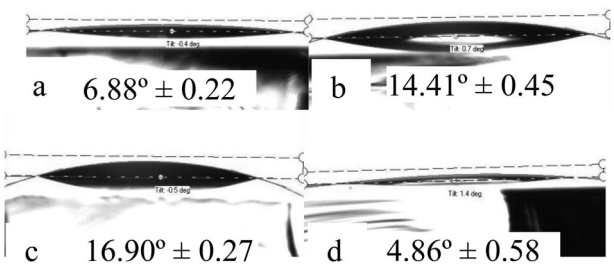

Fig. 4 Images with the water contact angle onto films with a configuration for the (a) glass/TiO_2; and glass/TiO_2 with (b) TCA, (c) TAA and (d) TDA.

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–CH_2– in the TAA molecule might be responsible for the higher hydrophobicity of this interface. From Fig. 4 it is possible to infer that TAA and TCA were the best modifiers for the TiO_2/P3HT interface and also that the worst modifier is TDA as confirmed by the smallest water contact angle (4.86 ± 0.58), demonstrating a more hydrophilic surface and thus a surface less compatible to the P3HT. The contact angle values are in agreement with TAS results and device's performance.

Additionally, the cross-sectional FEG-SEM images revealed no considerable differences in pore filling for TiO_2/P3HT films with and without the TAA modifier (see Fig. S1, ESI†).

Conclusions

This work has demonstrated the use of small organic molecules as interface modifiers in inverted TiO_2/P3HT hybrid solar cells. Although low V_{OC} values were obtained in these devices, our study pointed out a representative influence of the modification on the photovoltaic and optical properties of TiO_2/P3HT solar cells for all molecules used here. The best modifier was found to be the TAA molecule which leads to an improved exciton splitting and charge separation at the TiO_2/P3HT interface. Water contact angle measurements indicate that the interface modified by TAA is more hydrophobic and as a consequence more compatible with P3HT. These results were mirrored in improved overall cell performance for the TAA devices in terms of improved photocurrent generation and open circuit voltage compared to the control device where no modifier was used.

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